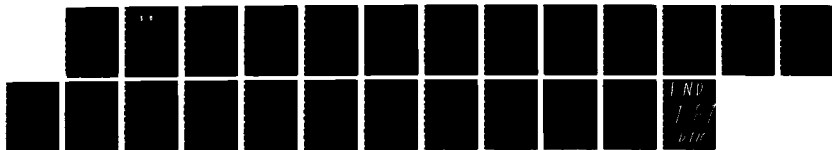
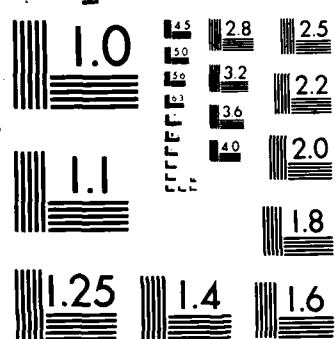


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DEPT OF CHEMISTRY AND BIOCHEMISTR C T LIN ET AL
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Emission Spectroscopic Evidence of Brønsted Acid
Sites in a Calcinated Vycor Glass

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EMISSION SPECTROSCOPIC EVIDENCE OF BRÖNSTED

ACID SITES IN A CALCINATED VYCOR GLASS

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ABSTRACT

The emission and excitation spectra of quinoline and 2,3-dichloroquinoxaline embedded in a calcinated (600°C) porous Vycor glass and dissolved in fluid solutions were recorded at various temperatures. The spectral characteristics and phosphorescence lifetimes of adsorbates were observed to be identical to those in 0.5 N H_2SO_4 solutions, indicating that H^+ is transferred from the surface to the N-heterocyclics. The strong surface-adsorbate interaction is further revealed by the dynamic study of adsorbates at 77 and 4.2K.

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I. INTRODUCTION

The identification of acid sites on open-structure supports (e.g., Vycor glass, zeolite, silica gel, alumina, etc.), especially the Brønsted acid sites is fundamentally important, not only for probing the catalytic mechanisms at these surfaces, but also for understanding the natural processes of chemical weathering and dissolution of silicate minerals, and of the activity of silica in biological systems. It is known⁽¹⁻³⁾ that the surface compositions of porous supports are the physisorbed and chemisorbed H_2O , and the silanol groups. The distributions of these species are very sensitive to the heat treatment of the solid supports. The interactions of adsorbate with open-structure supports arise normally from the non-specific interaction of the adsorbed molecule with the whole adsorbent and/or from the specific interaction with the active surface hydroxyls. Moreover, it is shown⁽⁴⁾ that the spectroscopic properties of embedded solutes in porous supports depend on their specific physical orientations while adsorbed on the porous surfaces (i.e., steric effects) and more importantly depend on which part or parts of the molecules that are actually experiencing the adsorptive effects (i.e., electronic interactions).

When open-structure supports are calcinated at $600^\circ C$, the bulk water is removed⁽¹⁾ completely from the porous and the remaining surface composition consist of trace amounts of chemisorbed H_2O and the surface silanols. Under this condition, one expects to detect only the specific interactions between the adsorbates and the $SiOH$ group of Vycor supports. Several experimental techniques⁽⁵⁻⁹⁾ and theoretical models⁽¹⁰⁻¹²⁾ have been used to investigate the possible proton donor-acceptor dynamics of porous supports, but the surface acid sites were evidenced^(5,7,8) only on the alumina and aluminum-contained surfaces. The effect of alumina on the surface acidity has also been discussed.⁽⁷⁾ For non-aluminum containing porous supports (e.g., Vycor glass, silica gel, etc.),

the investigations(12-15) focused mainly on the photophysical properties of embedded solutes. The hydrogen-bonding interaction between adsorbate molecules and surface hydroxyl groups on silica was noted,(16) but surface acidity has not been identified for the non-aluminum containing porous supports.

In this communication, we report the emission and excitation spectra of embedded N-heterocyclics (e.g., quinoline and 2,3-dichloroquinoxaline) in a calcinated (600°C) Vycor glass. The photophysical properties of N-heterocyclics are known⁽¹⁷⁾ to be extremely sensitive to the solvents used in fluid solutions. The observed changes in the spectral characteristics and phosphorescence lifetimes of embedded N-heterocyclics in a calcinated (600°C) Vycor glass relative to those dissolved in fluid solutions are used to probe the nature of Vycor glass. The dynamic interactions of the proton donor site of silanol group in porous Vycor glass with adsorbates will be illustrated.

II. EXPERIMENTAL

Code 7930 porous Vycor glass, containing $70 \pm 21 \text{ \AA}$ cavities and $(1.2 \pm 0.3) \times 10^{18}$ cavities/g,⁽¹⁸⁾ was purchased from the Corning Glass Company. The Vycor glass was calcinated at 600°C for 24 hours and then transferred promptly to the sample tube for adsorption. Quinoline, 2,3-dichloroquinoxaline (DCQ), methylcyclohexane (spectrophotometric grade, MCH) and 2,2,2-trifluoroethanol (TFE) were obtained from Aldrich Chemical Company. The first two compounds were purified according to standard procedures^(19,20) The last two solvents were used without further purification.

The fluid solution spectra were measured using 1×10^{-3} - $1 \times 10^{-5} \text{ M}$ solutions sealed in quartz ampules under a helium atmosphere. The embedded N-heterocyclics in Vycor glass were prepared using a low sample vapor pressure adsorption technique. This technique can be used to prevent the possibility of poisoning the surface active sites by the solvents. The N-heterocyclic sample

was introduced into a small quartz tube with one end open. This was then inserted into a large quartz tube where the calcinated Vycor glass has been preppacked at the end of the tube. The whole assembly was degassed and sealed under vacuum. The vapors of the N-heterocyclics gradually sublimed and became embedded in the porous Vycor glass.

The sample was placed inside a low temperature (77 K or 4.2 K) optical dewar. The 3130Å band of a PTI 100 watt high pressure mercury lamp was isolated using a 5 cm light path of an aqueous solution of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (200g/) with an UG11 Schott glass filter, and was used to excite the sample. The emission and excitation spectra were detected by an EMI 6256S photomultiplier tube in conjunction with an 1/2-meter Jarrell-Ash spectrometer. The phosphorescence decay was recorded using a Fabri-Tek series 1062 signal averager or a Biomation 805 waveform recorder interfaced with an Apple IIe computer. The computer was used to signal average the decay data which was then plotted via a graphics printing program. An electromechanical shutter which closes in less than one millisecond was driven by a HP 3312A function generator through a shutter drive unit (Vincent Associates, 100-B). The closing of the shutter and the sweeping of the signal averager were synchronized with the necessary electronics.

III. RESULTS AND DISCUSSION

A. Quinoline Embedded in a Calcinated Porous Vycor Glass

The emission spectra of quinoline embedded in porous Vycor glass recorded at 298, 77 and 4.2 K are displayed in the spectrum (D), (E) and (F) of Figure 1, respectively. At all temperatures studied, the spectrum of embedded quinoline is characterized by a single broad band and the band width is found to decrease as temperature decreases. The spectral peak maximum at 298, 77 and 4.2 K is located at 395, 385 and 385 nm, respectively (a 10 nm spectral blue shift for spectrum (E) relative to

spectrum (D) in Figure 1). These results suggest that a possible multiple sites adsorption and a structural relaxation through diffusional rotational motion probably occur for quinoline adsorbates on Vycor glass supports. The lifetime of this broad structureless emission was measured to be less than one msec (the shortest we can measure), i.e., only fluorescence but no phosphorescence emission is observed for quinoline adsorbates.

To ensure that the observed broad emission in the left-hand spectra of Figure 1 is not due to some photochemical products, we have carried out a prolonged irradiation experiment and have seen no noticeable spectral changes. The question is what is the origin of the observed broad emission? The possibilities are either the weakly bonded physisorbed quinoline on Vycor glass, the weak (or strong) hydrogen-bonded quinoline with the hydroxyl group of silanol or the quinolinium species resulting from a proton transferring of silanol to the adsorbed quinoline. If quinoline embedded in a calcinated porous Vycor glass results from a weakly bonded physisorbed species or a weak hydrogen-bonded quinoline, then the emission spectra in the left-hand portion of Figure 1 should resemble those of quinoline in a dilute solution of non-polar or polar solvents. The emission properties of quinoline in fluid solutions have been extensively investigated.^(17,19,21) In 3-methylpentane (non-polar solvent) at 77 K, quinoline shows only a well-resolved phosphorescence emission at $\lambda = 450-550$ nm and the lifetime was reported⁽¹⁹⁾ as $\tau = 1.04 \pm 0.05$ sec. For comparison, we have reproduced the emission spectrum of 1×10^{-4} M quinoline free base in MCH at 77 K which is displayed in Figure 1(A). The emission decay of Figure 1(A) has a lifetime of $\tau = 1.03$ sec which is in excellent agreement with that in 3-methylpentane reported by Anton et al.⁽¹⁹⁾ In EPA and in a solvent mixture of 3-methylpentane and ethanol (polar solvents) at 77 K, the emission spectra of quinoline show⁽¹⁹⁾ not only a well-resolved

phosphorescence at $\lambda = 450-550$ nm but also a well-structured fluorescence at $\lambda = 310-370$ nm. The fluorescence and phosphorescence have a comparable emission intensity. The phosphorescence lifetime of quinoline in polar solvents is significantly lengthened to $\tau = 1.29$ sec.⁽¹⁹⁾ It is clearly illustrated in the spectral characteristics and lifetime measurements that the broad emission observed for quinoline embedded in porous Vycor glass originates neither from the weakly bonded physisorbed species nor from the weak hydrogen-bonded quinoline.

Figure 1(B) shows the emission spectrum of 1×10^{-4} M quinoline in a solvent mixture of MCH and TFE (100:1) at 77 K where TFE is a stronger hydrogen bonding solvent with $pK_a = 12.4$ as compared to ethanol ($pK_a = 17$). The emission spectra in Figure 1(B) are quite distinct from those in Figure 1(A). Several observations should be mentioned: i) The phosphorescence intensity in Figure 1(B) is weak and the spectral band width is relatively broad as compared to those in Figure 1(A), ii) In both spectra 1(A) and 1(B), the phosphorescence emission seems to be located at the same wavelength, i.e., no significant spectral shift was observed, iii) The phosphorescence lifetime for quinoline in a solvent mixture of MCH + 1% TFE was measured as $\tau = 1.09$ sec which is essentially unchanged from its value in MCH solvent in the absence of TFE, and iv) For quinoline in a solvent mixture of MCH and TFE (100:1) at 77 K, a broad fluorescence with a peak maximum at 410 nm appears as shown in Figure 1(B). The spectral maximum of this broad fluorescence is found to shift gradually to the red by increasing the quinoline concentration. The same observation has been reported by Anton and Moomaw⁽¹⁹⁾ for quinoline in a solvent mixture of 3-methylpentane and hexafluoroisopropanol ($pK_a = 9.3$). They showed that this broad fluorescence is quite different from the excimer fluorescence of

quinoline reported by Blaunstein and Grant⁽²²⁾ and is also distinguishable from that of quinoline chloride in 3-methylpentane. Anton and Moomaw⁽¹⁹⁾ attributed this broad fluorescence spectrum as shown in Figure 1(B) to a quinolinium-like species formed during the lifetime of the excited singlet state of the close hydrogen-bonded quinoline. It is noted that the broad fluorescence emission in Figure 1(B) is quite similar to that observed in Figure 1(E) for quinoline embedded in porous Vycor glass.

Recently, we have reported^(23,24) that the emission spectrum of dibucaine (a tertiary amine local anesthetic drug) at 77 K originates from a chromophore of quinoline analogue. At pH = 0.6, the dibucaine·HCl in 0.5 N H₂SO₄ aqueous solution displays an emission spectrum of quinolinium analogue. Under the same acid condition, Figure 1(C) shows the emission spectrum of 1 x 10⁻⁴M quinoline in 0.5 N H₂SO₄ solution at 77 K. The spectrum is a single broad band with a peak maximum at $\lambda = 404$ nm. The broad band maximum tends to shift gradually to the red when the concentration of quinoline is increased. This broad emission band is identical to that observed for quinoline chloride⁽¹⁹⁾ in 3-methylpentane at 77 K. The lifetime of this broad emission resulting from the quinolinium species was measured to be less than one msec (the shortest we can measure) which is the same as that of spectrum 1(E) (i.e., quinoline embedded in a calcinated Vycor glass at 77 K). The similarities in the emission characteristics and lifetime of the broad spectral band in Figure 1(B), 1(C) and 1(E) suggest that the quinoline embedded in a calcinated porous Vycor glass could result in either a quinolinium ion or quinolinium-like species. The quinolinium ion is stable in both ground and excited states whereas the quinolinium-like species exists only in the excited state. The quinolinium-like species in its ground state is a strongly hydrogen-bonded quinoline. Anton and Moomaw explained⁽¹⁹⁾ that a strongly hydrogen-bonded

quinoline is excited to a strongly hydrogen-bonded excited state configuration followed by a partial or a total proton transfer to quinoline. This cationlike species then fluoresces with high quantum yield, and then the proton relaxes back to its stable ground-state hydrogen bonded configuration, i.e., a single proton transfer in an excited hydrogen-bonded quinoline results.

In order to confirm the quinoline embedded in porous Vycor glass is either a quinolinium ion or a quinolinium-like species (i.e., a strongly hydrogen-bonded quinoline), we have recorded the fluorescence excitation spectra of the broad emission in Figure 1(B), 1(C) and 1(E) and the results are displayed in the spectrum (A), (B) and (C) of Figure 2, respectively. In Figure 2(A), the excitation spectrum of the quinolinium-like fluorescence of quinoline in a solvent mixture of MCH and TFE (100: 1) at 77 K shows a well-resolved vibronic structure. The first absorption peak is at 314 nm which is also the most intense band. A similar spectral feature as shown in Figure 2(A) has also been reported⁽¹⁹⁾ for quinoline in a solvent mixture of 3-methylpentane and hexafluoroisopropanol (i. e., a strong hydrogen bonding solvent). In Figure 2(B) and 2(C), the excitation spectra for quinoline in 0.5 N H₂SO₄ solution and for quinoline embedded in a calcinated Vycor glass are broad and structureless with a spectral maximum at 317 nm. Both spectra (B) and (C) of Figure 2 show a broad shoulder band in the lowenergy side of the spectral maximum which is clearly not observed in the excitation spectrum of quinolinium-like species (Figure 2(A)). It is important to note that the excitation spectrum in Figure 2(B) is the same as that reported⁽¹⁹⁾ for quinoline chloride in 3-methylpentane at 77 K. The similarity between spectra (B) and (C) together with the difference between spectra (A) and (C) in Figure 2 suggest that quinoline embedded in porous Vycor supports is readily protonated, i.e.,

the Brønsted acid sites are presented in the calcinated (600°C) porous Vycor glass, at least for the strong base adsorbates such as quinoline and DOQ (which will be discussed below).

If the assignment of a ground state quinolinium ion associated with the embedded quinoline in Vycor glass is correct, the remaining question is why the fluorescence maximum observed for quinoline embedded in Vycor glass at 77 K is at $\lambda_{\max} = 385 \text{ nm}$ (Figure 1(E)) whereas that for quinoline in 0.5 N H_2SO_4 solution is at $\lambda_{\max} = 404 \text{ nm}$ (Figure 1(C)). At least two possible reasons can explain the observed spectral shifts for quinolinium ion in different environments. First, the possible structural relaxation through diffusional rotational motion for the embedded quinoline in Vycor glass is probably different from that of quinoline in 0.5 N H_2SO_4 fluid solution. This could account for the observed spectral shifts as those observed in the temperature effect of Figure 1(E) relative to Figure 1(D). Second, since the spectral maximum, λ_{\max} , in Figure 1(C) is very sensitive to the concentration of quinoline used, it is quite possible that the concentration of embedded quinoline in porous Vycor glass is much smaller than $1 \times 10^{-4} \text{ M}$ as used in the spectrum (C) of Figure 1. This result is consistent with the observation that we did not detect the excimer emission⁽²²⁾ for quinoline embedded in Vycor supports. If the second interpretation is true, the emission of embedded quinoline in porous Vycor supports must be greatly enhanced by the Vycor surfaces because under our experimental condition, we have difficulty of recording the emission spectrum of quinoline in 0.5 N H_2SO_4 solution for a concentration less than $1 \times 10^{-4} \text{ M}$.

B. DCQ Embedded in a Calcinated Porous Vycor Glass.

No phosphorescence emission was observed for quinoline embedded in porous Vycor glass as shown in Figure 1(D), 1(E) and 1(F). For the purpose of studying the phosphorescence dynamics of adsorbates, we recorded the emission spectra of DCQ molecules embedded in a calcinated (600°C) Vycor glass at 298, 77 and 4.2 K which are displayed in the Figure 3(d), 3(e) and 3(f), respectively. All spectra in the left-hand portion of Figure 3 show not only a broad structureless fluorescence with a spectral peak maximum at 408 nm but also a broad structured phosphorescence whose first emission peak is at 484 nm. The phosphorescence intensity is quite weak in Figure 1(d), and is probably quenched partially by the small amount of oxygen remaining in the vacuum sealed ampules at room temperature. It is analogous to the emission spectra of quinoline embedded in Vycor glass, the spectral band width of DCQ embedded in porous Vycor support is also shown to decrease as the temperature decreases, indicating a possible multiple sites adsorption for DCQ adsorbates. On the other hand, the fluorescence and phosphorescence emission maxima for DCQ embedded in porous Vycor supports show no apparent spectral shift on going from 298 K to 77 K and to 4.2 K, suggesting that the structural relaxation through diffusional rotational motion is not allowed for DCQ adsorbates on Vycor glass. The phosphorescence lifetime for the embedded DCQ in Vycor glass at 77 K was measured to be $\tau = 200$ msec.

To illustrate that a proton is transferred from the silanol group of the Vycor glass surface to the DCQ adsorbate when DCQ molecule is embedded in a calcinated (600°C) Vycor support, we display the emission spectra of DCQ in MCH, MCH + 1% TFE and 0.5 N H_2SO_4 fluid solutions at 77 K in the Figure 3(a), 3(b) and 3(c), respectively. In Figure 3(a), the emission spectrum of DCQ in MCH at 77 K shows only a well-resolved phosphorescence

structure whose origin is at 470 nm and lifetime was measured to be $\tau = 320$ msec. When 1% of TFE (a strong hydrogen-bonder) is introduced, a relatively weak and broad fluorescence with a band maximum at 415 nm is induced in the emission spectrum of DCQ in MCH + 1% TFE solution at 77 K as shown in Figure 3(b). The phosphorescence lifetime of DCQ in MCH + 1% TFE was measured as $\tau = 340$ msec which is slightly longer but is quite comparable to that observed for DCQ in MCH solution. In Figure 3(c), the emission spectrum of DCQ in 0.5 N H_2SO_4 solution at 77 K gives the following spectral features: i) the fluorescence intensity is stronger than that of the phosphorescence emission, ii) the band width of the phosphorescence emission is significantly broader than those in Figure 3(a) and 3(b), and the first spectral peak of the phosphorescence bands is at 481 nm, and iii) the phosphorescence lifetime for DCQ in 0.5 N H_2SO_4 solution at 77 K was measured to be $\tau = 190$ msec which is similar to that observed for DCQ embedded in porous Vycor glass at 77 K. In view of the similarity between the spectra (c) and (e) in Figure 3 and also their phosphorescence lifetimes, it is probable that a Brønsted acid site is present when DCQ is embedded in the calcinated (600°C) Vycor glass.

It is known⁽²⁵⁾ that at low temperature (4.2 K or lower) and when the spin-lattice relaxation rates between the zero-field spin sublevels of a phosphorescing triplet state are slow, a state of spin alignment (non-equal population of the zero-field sublevels) might be achieved as a result of the anisotropy in the intersystem crossing process. When this occurs, the relationship between a lifetime at 77 K to the lifetimes at 4.2 K is given by the equation⁽²⁶⁾

$$\frac{1}{\tau_{\text{at 77 K}}} = \frac{1}{3} \left(\frac{1}{\tau_1} + \frac{1}{\tau_2} + \frac{1}{\tau_3} \right) \quad (1)$$

where lifetimes on the right-hand side refer to the low temperature (4.2 K)

values for the three different zero-field spin sublevels of a triplet state. The phosphorescence emission of a $1 \times 10^{-4} \text{M}$ DOQ in MCH solution at 4.2 K display three distinct exponential decays and the phosphorescence lifetimes are $\tau_1 = 0.16 \text{ sec}$, $\tau_2 = 0.36 \text{ sec}$ and $\tau_3 = 2.8 \text{ sec}$. Using equation (1), the phosphorescence lifetime of DOQ in MCH solution at 77 K is calculated as $\tau = 320 \text{ msec}$ which is in excellent agreement with that observed for the phosphorescence emission in Figure 3(a). To test the possible spin alignment for the phosphorescence emission of embedded DOQ in Vycor glass at 4.2 K, we determined the decays for the phosphorescence emission in Figure 3(f) and we detected only a single exponential decay with $\tau = 200 \text{ msec}$ which is identical to that measured for the embedded DOQ in Vycor glass at 77 K. This observation indicates that the spin-lattice relaxation channels among the triplet spin sublevels are fast for the embedded DOQ in the calcinated Vycor glass at 4.2 K. The fast spin-lattice relaxation for the embedded DOQ at 4.2 K might be simply due to the intrinsic properties of the protonated DOQ or due to the strong surface-adsorbate interactions.

IV. REMARKS

For adsorbates embedded in the non-aluminum containing porous supports, the binding of molecules with π -systems or with lone pair electrons is believed⁽¹³⁾ to be largely by hydrogen-bonding to the silanols or to the physisorbed water molecules. Our experimental results have shown that the Brønsted acid sites are clearly evidenced in the calcinated (600°C) Vycor glass when quinoline and DOQ are embedded. In fact, Basila⁽¹⁶⁾ has illustrated that the protons in surface silanol groups have an even greater positive character than those in molecular silanol groups. On the surface, there is an increased delocalization of the oxygen lone pair electrons through π -bonding with the vacant d orbitals of both

the bonded silicon atom of the surface silanol group and an adjacent non-bonded silicon atom. The increase in the delocalization of the lone pair electrons of oxygen would cause a larger shift of the bonding electrons toward the oxygen of the OH in surface silanol groups thereby making the proton more positive than in molecular silanol group.

We have shown⁽²⁷⁾ that phosphorescence-Microwave Double Resonance (PMDR) spectroscopy is an extremely sensitive technique for studying the different sites in molecular solid at 4.2 K. This technique can certainly be extended to study the possible multiple adsorption sites for embedded N-heterocyclics in Vycor glass if a spin-alignment is retained in the systems studied. The spin-lattice relaxation is found to be fast for the triplet state of DCQ embedded in the porous Vycor glass at 4.2 K. However, the phosphorescence decays of benzo[c]cinnoline and benzophenone embedded in Vycor glass at 4.2 K are observed⁽²⁸⁾ to display a non-exponential decay. The study of the different adsorption sites for the triplet adsorbates at 4.2 K using PMDR technique is currently in progress in our laboratory.

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FIGURE CAPTIONS

Figure 1. Right: emission spectra of quinoline dissolved in MCH (A), MCH + 1% TFE (B) and 0.5 N H₂SO₄ (C) at 77 K. All spectra were taken with a concentration of 1×10^{-4} M. Left: emission spectra of quinoline embedded in porous Vycor glass at 298 K (D), 77 K (E) and 4.2 K (F).

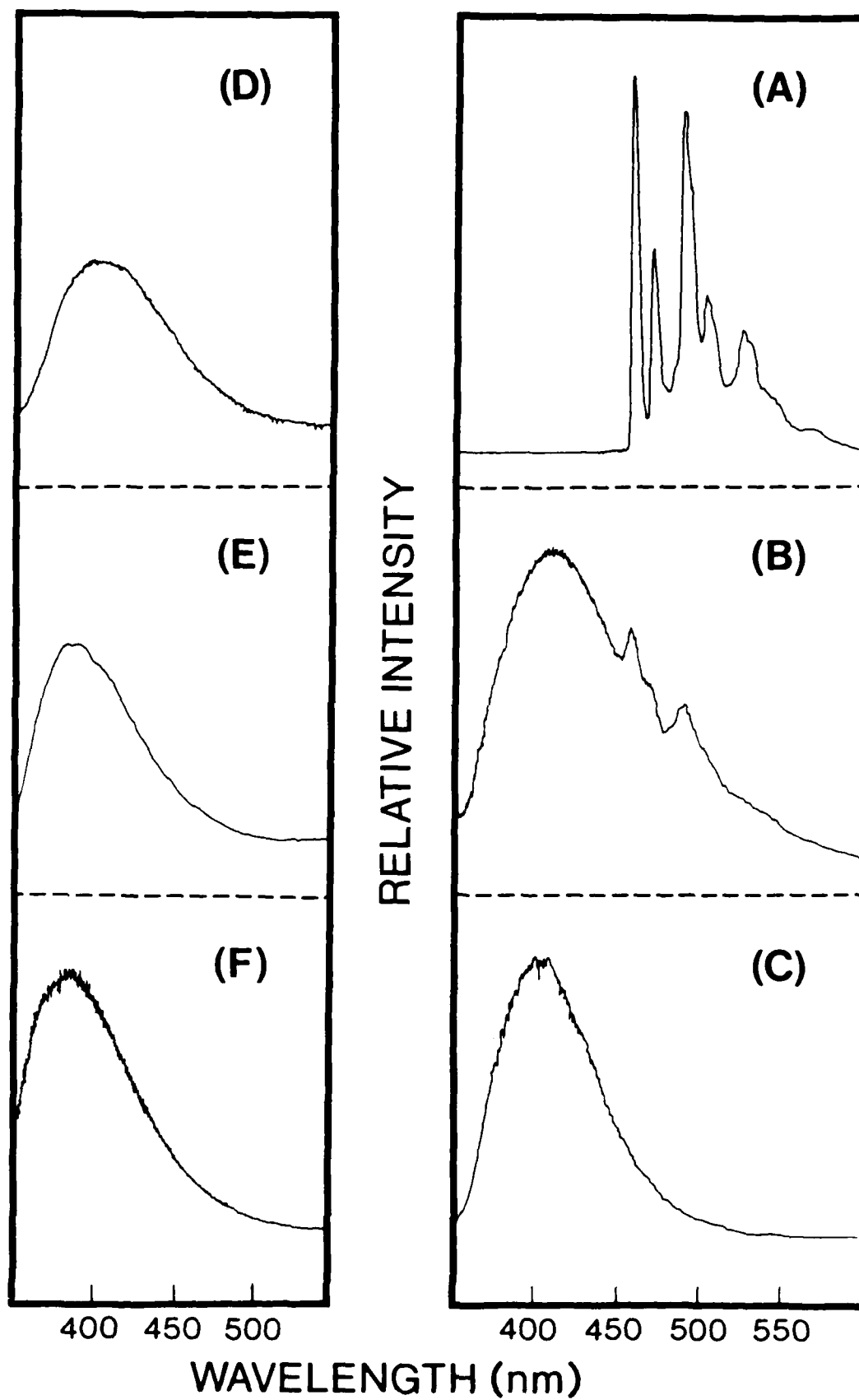
Figure 2. Fluorescence excitation spectra of quinoline dissolved in MCH + 1% TFE (A), 0.5 N H₂SO₄ (B) and embedded in porous Vycor glass (C) at 77 K. Spectra (A) and (B) were taken with a concentration of 1×10^{-4} M.

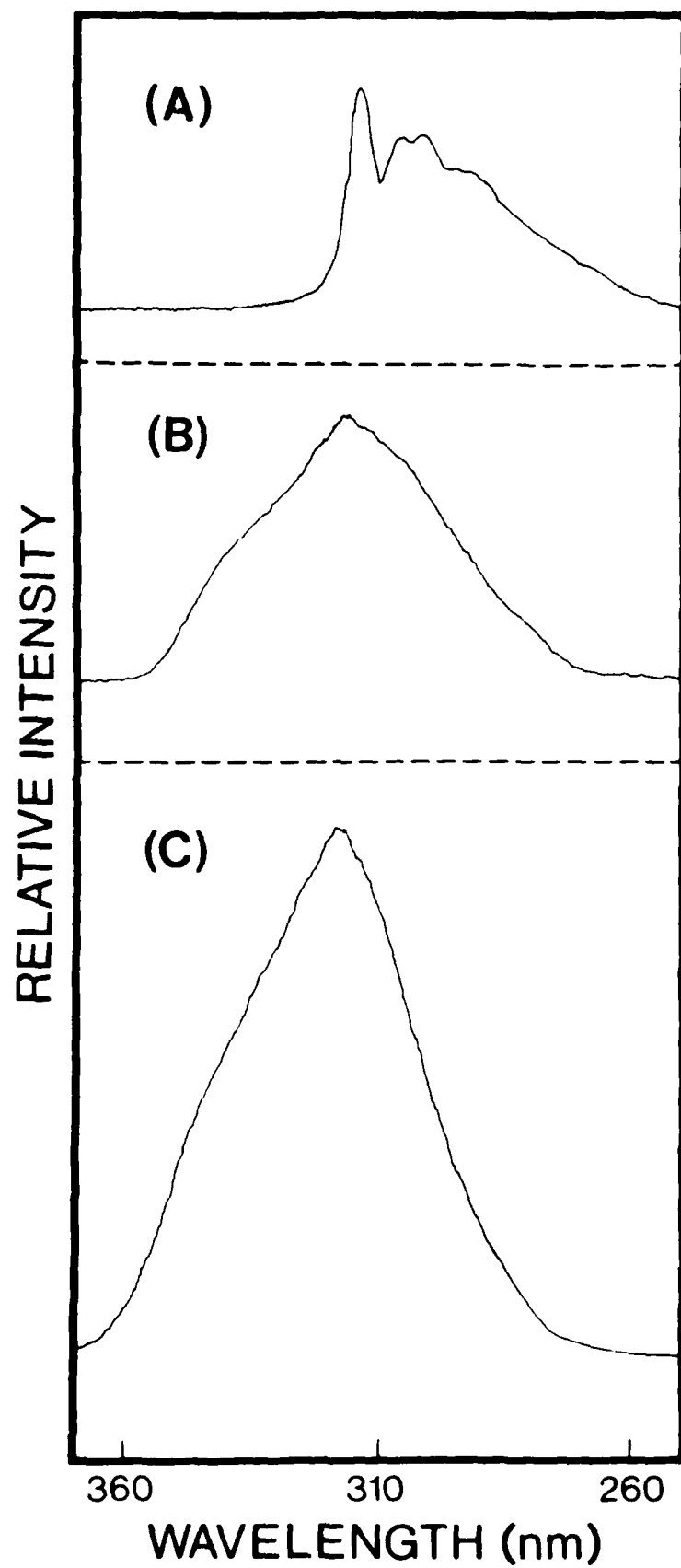
Figure 3. Right: emission spectra of DCQ dissolved in MCH (a), MCH + 1% TFE (b) and 0.5 N H₂SO₄ (c) at 77 K. All spectra were taken with a concentration of 1×10^{-4} M. Left: emission spectra of DCQ embedded in porous Vycor glass at 298 K (d), 77 K (e) and 4.2 K (f).

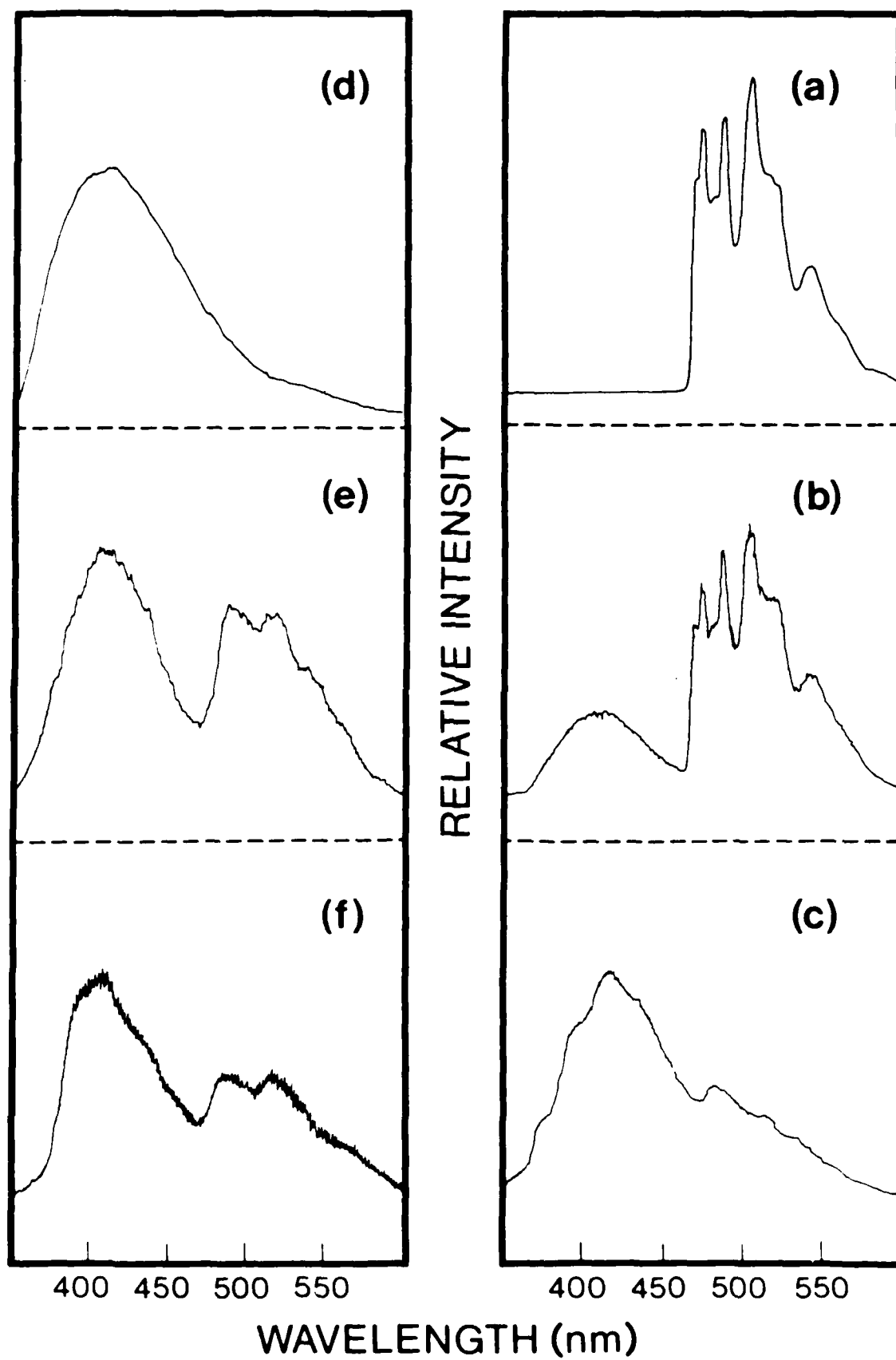
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